Radiometric Measurements of the Ionization Constants of Methyl Orange and Phenolphthalein

DISSERTATION

Submitted to the Board of University Studies of the Johns Hopkins University in Conformity with the Requirements for the Degree of Doctor of Philosophy

BY

MAX G. PAULUS

Baltimore, Maryland

June, Nineteen Hundred and Fifteen

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RADIOMETRIC MEASUREMENTS OF THE IONIZATION CONSTANTS OF METHYL ORANGE AND PHENOLPHTHALEIN

THE quantitative development of the theory of indicators and the application of the ionization constants of indicators to problems of volumetric analysis, of which an exhaustive study has been made by Noyes[1] and Bjerrum[2], makes it extremely desirable to know accurately the ionization constants of a series of indicators. But unfortunately, as Noyes points out, our knowledge of the indicator constants at present available is for the most part inexact, and further careful investigations are desired. In fact, a perusal of the work of previous investigators will show, in some cases at least, that the results of a series of measurements will vary by as much as 400%.

Purpose of this Investigation

In this paper it is desired to present the results of a quantitative investigation of the ionization constants of two of the most important indicators—methyl orange and phenolphthalein. A new method of attacking this problem is developed which is especially applicable to two-colored indicators, and which, in the mind of the writer at least, is freer from limitations and objections than any of the previous methods.

Historical

Extensive preliminary investigations upon the color changes exhibited by indicator solutions of known hydrogen

[1] Jour. Amer. Chem. Soc., 32, 815 (1910).
[2] Ahr. Versamm., 21, 1 (1914).

ion concentrations were first made by Friedenthal[1], Salessky[2], Fels[3] and Salm[4]. Their results are given in the form of tables showing roughly the hydrogen ion concentration at which a large number of indicator solutions undergo change in color. Salm[5], utilizing the principle that the ionization constant of an indicator is equal to the hydrogen ion concentration at which the indicator is 50% dissociated, determined the ionization constants of seven of the more important indicators. The point at which the indicator is one-half transformed into its salt was determined by a colormetric method; the hydrogen ion concentrations were determined by E. M. F. measurements. McCoy[6], by the use of a colormetric method, determined the hydrolysis constant of phenolphthalein. The mean value obtained was 1.55×10^{-4}. From the mean value of the hydrolysis constant and the known ion product for water, the value of the ionization constant of phenolphthalein was found to be 7.5×10^{-11}. In one series of measurements the value of the hydrolysis constant varied from 0.66×10^{-4} to 2.9×10^{-4}, a difference of as much as 400%. The bleaching of phenolphthalein solutions by an excess of alkali was investigated, and also a brief treatment upon the use of phenolphthalein as an indicator is given. A quantitative study of phenolphthalein was also made by Hildebrand[7] and Wegscheider[8]. Hildebrand made use of a spectrum photometer to determine the concentration of the colored component. His method is undoubtedly the most exact of all the methods previously employed. Wegscheider[8] followed essentially the colormetric method developed by McCoy[9]. He comes to the conclusion that the assumption that phenolphthalein acts as a monobasic acid is erroneous. The variation in the constants obtained were explained by

1 Zeit. Electrochem., 10, 113 (1904).
2 Ibid., 10, 204 (1904).
3 Ibid., 10, 208 (1904).
4 Ibid., 10, 344 (1904).
5 Zeit. Physik. Chem., 57, 485-497 (1907).
6 Amer. Chem. Jour., 31, 503 (1904).
7 Zeit. Electrochem., 14, 349 (1908).
8 Ibid., 14, 510 (1908).
9 Loc. cit.

regarding phenolphthalein as a dibasic acid. Rosenstein[1] confirms this conclusion, and furthermore shows that the colored form of the indicator is produced in appreciable quantity only when the second hydrogen of the indicator acid is replaced by the base. The effect of neutral salts upon the fraction of the indicator transformed was also carefully investigated. It was found that the value of the ionization constant was doubled by increasing the total salt concentration from 0.03 to 0.40 normal.

Paranitrophenol is a much stronger electrolyte and its constant can be determined by conductivity methods. In this way Bader[2] obtained the value 1.2×10^{-7}. Later Hantzsch[3] obtained the value 0.96×10^{-7} by the same means.

The application of the theory of indicators to problems of volumetric analysis was first given in a brief way by McCoy[4] and Salm[5]. An exhaustive study of this very important question was made by Noyes[6] and Bjerrum[7].

The Apparatus

A detailed description of the various parts of the apparatus will be given, with emphasis laid especially upon construction and experimental manipulation. Careful construction of the component parts is absolutely essential in work of this character, involving as it does the measurement of energy radiations of extremely small intensities.

Light of uniform intensity is supplied by a Nernst glower. After being rendered parallel by means of a lens A, the light passes through the solution under investigation. The solution is contained in gold-plated brass cells, provision being made by means of a sliding carriage to place first one cell and then the other in the path of the light. This steel carriage is mounted upon a heavy steel standard, which holds

1 Jour. Amer. Chem. Soc., 34, 1117 (1912).
2 Zeit. Physik. Chem., 6, 297 (1890).
3 Ber., 32, 3070 (1899).
4 Loc. cit.
5 Loc. cit.
6 Loc. cit.
7 Loc. cit.

also the Nernst glower and the lenses A and B, and is so adjusted that either cell can be made to occupy exactly the same position in the path of the light. By means of the lens B the beam of light is then focused upon the slit S^1 of the spectroscope. From the slit S^1 the beam of light is reflected by means of a right-angle prism P into the lens C. The slit S^1 is placed at the focus of the lens C and thus parallel light falls upon the grating G. The dispersed light reflected back through the lens C passes over the top of the prism P and is focused upon the second slit S^2 of the spectroscope. The beam of light is then focused by means of another lens of short focal length upon the junction of the radiomicrometer. By the use of a metal screen interposed in the path of the light between the Nernst glower and the lens A, the light could be made to fall upon the junction of the radiomicrometer only long enough to read the deflection produced.

The Nernst Glower: The Nernst glower was connected in series with a ballast, a variable resistance, an ammeter, and a 120-volt storage battery circuit. Since the resistance of any conductor is affected by temperature changes, in order to prevent variations in the intensity of the light source due to this cause the Nernst glower was inclosed in a box of heavy asbestos board, thereby preventing, as much as possible, the rapid cooling of the filament by air-drafts. At the same time the current was always carefully maintained constant by means of the variable resistance. This asbestos box was attached to the steel standard by a sort of universal joint, by means of which it was possible to focus the image of the glower quickly and accurately upon the slit S^1 of the spectroscope. The method employed for determining the percentage transmission of a given depth of solution for a given wavelength of light, made it absolutely necessary that the light source be maintained at uniform intensity for short intervals of time.

The Cells: The cells which contained the solution to be investigated consisted of two brass cylinders neatly telescoping into one another. In the ends of each of these cylinders were sealed, by means of Wood's metal, two plano-parallel

lenses. These lenses were made by Brashear of the best optical glass. They were all made of exactly the same thickness out of the same kind of glass, and their surfaces were parallel to within 5 wavelengths of light. In order to set accurately the distance between the glass ends, which determined the depth of solution in the path of the light, a carefully threaded nut was made to screw over the outside cylinder. The top of this nut fitted neatly with a flange on the inside cylinder, and by simply turning the nut in the proper direction the inside cylinder could be raised or lowered. The periphery of this nut was divided into one hundred equal divisions by means of the dividing engine. Since one full revolution of the nut changed the distance between the glass ends by exactly one millimeter, it was possible to obtain to one-hundredth of a millimeter directly any desired distance between the glass ends.

Great difficulty was experienced in setting the glass plates into the cylinder ends with Wood's metal, since the fusible metal on setting often warped and distorted the plates to such a degree that they became unfit for use. When the lenses were secured in the ends of the cylinder they were always tested in the following manner: The cylinders were telescoped together so that the inside glass surfaces touched, and the lenses were then tested as to their parallelism by the character of the interference fringes produced in monochromatic light.

The differential method[1] employed for determining the transmission for any given depth of solution made the use of two cells absolutely necessary. These cells had to be made as nearly alike as possible, so far as their optical properties were concerned. The methods used and the precautions taken to secure this result have already been described. As a final assurance of the optical identity of the two cells a depth of water equal to 5mm. was placed in each cell, and the transmissions as measured by the deflections of the radiomicrometer were determined when each cell was placed in the

[1] See page 19.

path of the light. These measurements were made for many wavelengths of light throughout the entire region of the spectrum studied. Since equal depths of water absorb to the same amount if the light passing through each cell suffers the same amount of reflection and absorption due to the glass ends, then the deflections of the radiomicrometer produced by light of the same wavelength passing through each cell would be the same. That such a result was obtained can be seen from a consideration of Table I. In columns 2, 3, 5 and 6 are recorded the actual scale deflections of the radiomicrometer for wavelengths of light recorded in columns 1 and 4.

Table I

λ = Å. U.	Cell A.	Cell B.	λ = Å. U.	Cell A.	Cell B.
4546	4	4	8029	125.0	125.0
4797	8.2	8.2	8275	127.0	127.5
5047	14.2	14.5	8520	129.0	129.0
5298	22.0	22.5	9009	129.5	130.0
5548	31.5	31.5	9497	115.5	115.0
5797	41.5	41.7	9982	105.5	106.0
6046	50.5	50.5	10465	113.5	114.0
6295	60.7	60.5	10946	108.5	108.0
6543	70.5	71.2	11424	69.0	69.0
6792	86.7	86.5	11900	51.5	52.0
7041	100.5	100.0	12373	56.0	56.0
7290	107.7	107.7	12843	53.5	54.0
7536	114.0	114.5	13314	34.0	34.0
7784	120.5	120.5	13775	11.0	10.7

Considerable trouble was often caused by the appearance of opalescent streamers in some of the solutions used when these solutions were allowed to remain in the cells for any length of time. These streamers appeared to arise from the very small surface of the Wood's metal exposed to the solution, and were very probably due to some electrolytic action between the metallic constituents present. After the glass ends were properly set the cells were always electroplated with a light coat of silver and a very heavy coat of gold; but even this failed at times to prevent entirely the formation of streamers. A thin coat of replica solution applied to the surface of the exposed fusible metal very effectively eliminated

this difficulty. The formation of streamers can change the transmission of a solution as much as 10%.

The Spectroscope: The spectroscope was constructed in the physical laboratory under the direction of Professor John A. Anderson. The mounting was of the Littrow type, the same lens serving to render the light incident upon the grating parallel, and also to focus the diffracted light upon the second slit of the spectroscope. A four-inch Brashear lens was used, having a focus of 30 inches. Both slits were of the bilateral type.

Mechanically the instrument was most carefully constructed. The screw which rotated the grating through definite angles was very accurately ground. This was attached, by means of a heavy brass shaft, to a four-inch drumhead, which was divided into 500 equal divisions. The screw was of such a pitch that one complete revolution of the drumhead changed the wavelength of light falling upon the second slit by approximately 500 Ångström units. A counter attached to the brass shaft by gear wheels registered the number of complete revolutions.

A calibration curve was prepared for the readings given by the drumhead, the wavelength corresponding to any given reading being calculated from the known grating space by the formula:

$$\lambda = 33{,}866.7 \sin \frac{3000T + 6R}{3500}$$

in which T is the number of complete revolutions and R the actual reading on the drumhead. This calibration was then checked by the positions of prominent lines in the emission spectra of sodium, mercury, and lithium.

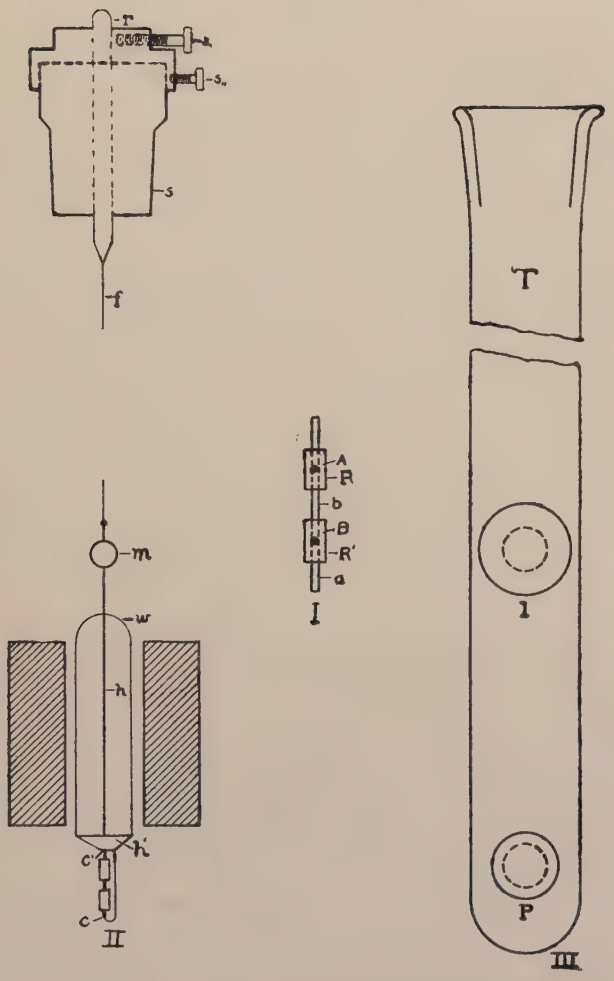
The Grating: A four-inch Anderson grating was used. This particular grating was selected on account of the brightness of its first order spectrum, which was especially desirable in this investigation, since the use of color screens to cut out the higher orders was unnecessary. Energy measurements made on the first order spectrum on either side of the central

image showed that one side was slightly more intense. This side was accordingly used throughout the following work:

Glass is opaque to wavelengths of light below $\lambda = 0.35\ \mu$. Since light of wavelength l in the first order is superimposed by light of wavelength $l/2$ in the second order, it follows that the first order spectrum is pure up to wavelength $\lambda = 0.70\ \mu$. As far as energy measurements with the radiomicrometer are concerned, the first order spectrum is really pure up to wavelength $\lambda = 1.2\ \mu$, *i. e.*, light of wavelength $\lambda = 0.6\ \mu$ of the second order is not sufficiently intense to give a detectable deflection of the radiomicrometer. This was determined experimentally in the following manner: A depth equal to 10 millimeters of a solution of copper sulphate which was nearly saturated gave appreciable deflections of the radiomicrometer only between wavelengths $\lambda = 0.4\ \mu$ and $\lambda = 0.6\ \mu$ of the first order spectrum. Measurements were then made with this same solution in the path of the light from wavelength $\lambda = 0.8\ \mu$ to $\lambda = 1.2\ \mu$. No deflections of the radiomicrometer were obtained. Since the second order spectrum from wavelength $\lambda = 0.4\ \mu$ to $\lambda = 0.6\ \mu$ overlaps this region, and since the solution is transparent to these wavelengths of light, it follows that the second order spectrum in this region is not sufficiently intense to give a detectable deflection of the radiomicrometer. In other words, the first order spectrum is pure as far as energy measurements are concerned for all wavelengths of light below $\lambda = 1.2\ \mu$. This investigation was carried out between wavelengths $\lambda = 0.5\ \mu$ and $\lambda = 0.6\ \mu$.

The Radiomicrometer: The radiomicrometer was constructed and built by Dr. E. J. Shaeffer[1]. It consisted essentially of a thermo-junction attached to a loop of non-magnetic wire which was suspended in a magnetic field by means of a very fine quartz fiber f. The whole was suspended in the tube T from the torsionhead S. The construction of the torsionhead made it possible to raise or lower the suspended system, or to turn it through a definite angle. Energy

[1] Jour. Amer. Chem. Soc., 37, 776 (1915).



radiations falling upon the junction *A* set up an electric current in the loop, causing this to turn through a definite angle which is measured by a beam of light reflected from the mirror.

The junction was of the compensating type. Arm *a*, composed of an alloy of 97 parts of bismuth and 3 parts of antimony, is soldered at *A* to another arm *b*, composed of 95 parts of bismuth and 5 parts of tin. This arm in turn is soldered

at B to another arm a' similar to a. These arms are approximately 1 mm. wide by 3 mm. long, and of extreme thinness. When both junctions are simultaneously heated the current set up in one junction is exactly opposed by the current set up in the other, and thus no deflection of the loop is produced. The advantages of such an arrangement are obvious. Temperature changes with the single junction type of instrument cause a most troublesome drift of the reflected beam. The compensating junction almost entirely eliminates this difficulty. Each junction is attached to a vane of very thin tinfoil, each having the same area (approximately 4 sq. mm.). These vanes are blackened by a solution of lampblack in thin shellac. Especial care was taken to reduce the weight of the junction to a minimum, as low heat capacity insures a quick rise to the maximum deflection, and a quick return to the zero point of the reflected beam. Some idea may be gained as to the weight of the junctions themselves when the whole suspended system, excluding the mirror, which was indeed only a fragment of silvered glass, weighed in one case only 0.0029 grams. The beam of light from the second slit of the spectroscope was, of course, focused upon one of these vanes.

The loop of non-magnetic wire was first etched by means of dilute nitric acid to remove any iron from the dies used in drawing the wire. This precaution is necessary to prevent magnetic control, which, when appreciable, renders the instrument unfit for accurate measurements of energy. The diamagnetic materials composing the junction are placed at right angles to the lines of force of the magnetic field, and are also placed outside of the field. In this way spurious effects are reduced to a minimum. The glass supports h and h' are really glass tubes of extremely small diameter. Glass rods of the same diameter would, of course, have greater weight.

The quartz fiber f which supported the system had a length of $11\frac{3}{4}$ inches. A very long fiber was used to secure greater stability of the suspended system.

The glass tube in which the instrument was suspended was fitted with a glass window p, through which the light

from the slit S^1 was focused upon the junction. The lens l opposite the mirror m had a focus of approximately 12 feet. This length of reflected beam is especially desirable, since the actual deflections of the mirror are of such a small magnitude.

The heavy iron base upon which is fastened the tube T and also the permanent magnet, the pole pieces of which are represented in Fig. 2, was insulated from vibrational disturbances by many thicknesses of felt and also wads of raw cotton. The whole was inclosed in a large blackened box, in order to protect more securely the instrument from air-drafts. That portion of the glass tube about the junction was inclosed in a cylinder containing fine lead shot, provision being made by means of a pasteboard tube so that the light could still be focused upon the junction A. Owing to the high heat capacity of the large mass of metal, temperature changes within the tube about the junction could only take place very slowly.

Theoretical Discussion

The first theory explaining the color change of indicators, and the varying degrees of sensitiveness shown by different indicators towards weak acids and bases, we owe to Ostwald.[1] An indicator, as Ostwald points out, is either a weak acid or a weak base, and is therefore capable of salt formation. The indicator itself is consequently slightly ionized, but the salt into which it is transformed by the addition of acid or alkali, as the case may be, is highly ionized. This change in the ionic condition is coincident with a change in color; and Ostwald was led to the conclusion that the two were related to each other as cause and effect. This conclusion was all the more justified in consideration of an elaborate investigation[2] which Ostwald had made upon some 300 inorganic substances in solution. In this work he showed that the color changes produced by the addition of water to dry inorganic salts were almost certainly due to changes from the

1 Lehr. der. Allg. Chem., 1, 799 (1891).
2 Ztschr. Phys. Chem., 9, 579 (1892).

molecular into the ionic condition. Thus, all salts with the same colored cation and colorless anions showed identical absorption spectra in dilute solutions.

More recent work, however, upon the relations between the color and the structure of organic compounds, especially that of Bernthsen[1], Nietzi and Burckhart[2], and Hantzsch[3], shows that the color change is not due primarily to a simple change in ionization, but to deep-seated changes in the constitution of the molecule of the indicator. In view of this theory an indicator, in all probability, exists as two tautomeric substances having different structural types; the ionization constants of the two tautomers and the stability constant being such that one greatly predominates when the indicator exists as a weakly ionized acid or base, the other predominating when the indicator exists as a strongly ionized salt. Or, as Stieglitz[4] has pointed out, although the change in ionization is not the direct cause of the color change the two, color change and ionization, are practically coincident.

Although the theory explaining the color change of indicators is probably the most interesting, the theory underlying the sensitiveness of indicators in its application to acidimetry and alkalinity is by far the most important. Even in the light of the present theories on the behavior of indicators, Ostwald's conception of sensitiveness is still essentially correct. According to Ostwald the sensitiveness of an indicator depends chiefly upon the numerical size of its ionization constant as an acid or base. In view of the present theory explaining the change in color of indicators, the ionization constant to be considered not only depends upon the ionization constants of the two tautomeric forms present, but also upon the stability constant of the two tautomers[5].

[1] Chem. Ztg., 1956 (1892).
[2] Ber. d. Chem. Ges., 30, 175 (1897).
[3] Ibid., 32, 583, 3085 (1899), etc.
[4] Jour. Amer. Chem. Soc., 25, 1112 (1903).
[5] For a much more comprehensive discussion of this matter see A. A. Noyes, Jour. Amer. Chem. Soc., 32, 813 (1910).

Methyl Orange

Accepting this conception of sensitiveness, methyl orange being in reality a weak base[1], exists in solution in the two tautomeric forms:

$$NaSO_3 \cdot C_6H_4 \cdot N = N \cdot C_6H_4 \cdot N(CH_3)_2HOH \rightleftarrows$$
$$NaSO_3 \cdot C_6H_4 \cdot NH \cdot N = C_6H_4 = N(CH_3)_2OH \quad (1)$$

Each of these tautomers would be ionized according to the equilibrium equations:

$$NaSO_3 \cdot C_6H_4 \cdot N = N \cdot C_6H_4 \cdot N(CH_3)_2HOH \rightleftarrows$$
$$NaSO_3 \cdot C_6H_4 \cdot N = N \cdot C_6H_4 \cdot N\overset{+}{(CH_3)_2}H + \overset{-}{OH} \quad (2)$$

and

$$NaSO_3 \cdot C_6H_4 \cdot NH \cdot N = C_6H_4 = N(CH_3)_2OH \rightleftarrows$$
$$NaSO_3 \cdot C_6H_4 \cdot NH \cdot N = C_6H_4 = N\overset{+}{(CH_3)_2} + \overset{-}{OH} \quad (3)$$

In a pure aqueous solution of methyl orange the equilibrium relation of equation (1) is such that the azo-base is present in greatly predominating quantity. However, owing to the fact that the quinoid base has a very much larger ionization constant, the quinoid salt is formed in very much larger proportion when the mixture is neutralized with an acid. Representing the three fundamental equations of equilibrium by the following symbols:

$$\frac{QOH}{AzOH} = k. \quad (1)$$

$$\frac{\overset{+}{Az} \times \overset{-}{OH}}{AzOH} = K_{AzOH}, \quad (2)$$

$$\frac{\overset{+}{Q} \times \overset{-}{OH}}{QOH} = K_{QOH}, \quad (3)$$

A general expression can then be derived, as has been done by A. A. Noyes[2], expressing the equilibrium relations between

1 Jour. Amer. Chem. Soc., 25, 1121 (1903).
2 Loc. cit.

the two tautomeric bases and their ions. Multiplying (1) by (3) and adding (2) to the product, we get:

$$\frac{\overset{+}{Q} \times \overset{-}{OH} + \overset{+}{Az} \times \overset{-}{OH}}{AzOH} = k \times K_{QOH} + K_{AzOH},$$

and substituting for AzOH in the denominator its value $\frac{AzOH + QOH}{1 + k}$, obtained from (1), we have:

$$\frac{\overset{-}{OH}(\overset{+}{Az} + \overset{+}{Q})}{AzOH + QOH} = \frac{k \times K_{QOH} + K_{AzOH}}{1 + k} = K_i. \qquad (4)$$

For a satisfactory two-color indicator the sum (AzOH + QOH), must be substantially identical with AzOH; and the sum $(\overset{+}{Q} + \overset{+}{Az})$ must be substantially identical with $\overset{+}{Q}$, and thus equation (4) reduces to:

$$\frac{\overset{-}{OH} \times \overset{+}{Q}}{AzOH} = K_i, \qquad (5)$$

which is essentially the equation derived by Stieglitz[1] expressing the dynamic condition of ionization of methyl orange.

By combining this equation with that of the ion product for water, $\overset{+}{H} \times \overset{-}{OH} = K_w$, we have:

$$\frac{\overset{+}{H} \times AzOH}{Q^+} = \frac{K_w}{K_i} = K_{(hydrolysis)} \qquad (6)$$

which is in reality the familiar equation of Walker[2], $(\frac{acid \times base}{salt} = k)$ when the base is weak as in the case of methyl orange and the acid is highly ionizable.

The method first tried was as follows: A solution of methyl orange containing 3.973×10^{-4} gram-molecules per liter, and also a solution of sulphuric acid containing 3.088×10^{-4} gram-molecules per liter were prepared. From these two stock solutions the following test solutions were made:

[1] Loc. cit.
[2] Ztschr. Phy. Chem., 4, 324 (1889).

Solutions

I	50 cc. methyl orange, diluted to 100 cc.
II	50 cc. methyl orange, 5 cc. sulfuric acid, diluted to 100 cc.
III	50 cc. methyl orange, 10 cc. sulfuric acid, diluted to 100 cc.
IV	50 cc. methyl orange, 15 cc. sulfuric acid, diluted to 100 cc.
V	50 cc. methyl orange, 20 cc. sulfuric acid, diluted to 100 cc.
VI	50 cc. methyl orange, 30.9 cc. sulfuric acid, diluted to 100 cc.
VII	50 cc. methyl orange, 35 cc. sulfuric acid, diluted to 100 cc.
VIII	50 cc. methyl orange, 1.0 cc. conc. sulfuric acid, diluted to 100 cc.
IX	50 cc. methyl orange, 2.0 cc. conc. sulfuric acid, diluted to 100 cc.

A large excess of acid was added to solutions 8 and 9 in order to suppress hydrolysis practically completely, and thus to insure a complete conversion of the azo-base into the quinoid salt.

The percentage transmissions for a depth equal to 20 mm. of each of these solutions were then determined for various wavelengths in the yellow-green region of the spectrum. In order to obviate any error arising from reflection from the glass ends with which the cell was fitted, and also to avoid corrections for the difference in refraction of glass and solution, a differential method was employed. This method made the use of two cells necessary. These cells were constructed as nearly alike as possible, as far as their optical properties were concerned (see page 8). If it were desired to obtain the percentage transmission for a depth of solution equal to 20 mm., 21 mm. of solution would be placed in one cell and 1 mm. of solution in the other. Light of uniform intensity was then passed through each cell separately, and the deflection of the radiomicrometer, which is a measure of the intensity of the transmitted light in each case, was noted. The deflection of the radiomicrometer produced when the deeper layer was placed in the path of the light, divided by the deflection obtained when the more shallow layer was placed in the path of the light, gives the percentage transmission of $21 - 1$, or 20 mm. of solution. This may be made clearer from the following consideration[1]. Suppose we have a solution of depth l' and let the intensity of the incident light be I_o, and

[1] See also Carnegie Monograph No. 190, pg. 62.

that of the transmitted light I_I then from theoretical considerations we have the following relation:

$$I_I = I_o e^{-kl'} \qquad (7)$$

Suppose a depth of l'' of the same solution be considered, and let the new transmission be I_{II}, then:

$$I_{II} = I_o e^{-kl''} \qquad (8)$$

Dividing (7) by (8):

$$I_I/I_{II} = e^{k(l''-l')} \qquad (9)$$

But the actual percentage transmission given by the same solution of depth $l' - l''$ is given by:

$$I/I_o = e^{-k(l'-l'')} = e^{k(l''-l')}, \qquad (10)$$

$$\text{or} \quad I_I/I_{II} = I/I_o. \qquad (11)$$

The percentage transmissions of solutions 1 to 9 obtained for various wavelengths are given in Table II.

Table II

	I/I_o for depth of solution = 20 mm.									Average of VIII and IX.
λ=Å.U.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	
5748	84.6	---	71.9	65.1	57.7	49.1	46.7	9.5	8.4	8.95
5798	90.0	85.6	79.3	73.3	70.0	62.2	61.0	22.1	22.1	22.1
5847	91.4	---	84.6	81.4	77.9	70.3	---	35.7	35.7	35.7

The data given in Table II are sufficient to calculate the concentrations of the two absorbing components present at equilibrium in solutions 2–7 inclusive, *i. e.*, the concentrations of the azo-base and of the quinoid salt. Suppose light of intensity I to pass through an absorbing solution of thickness l, the solvent itself having no absorption in the particular region under investigation, then the rate of change of intensity is expressed by the formula $dI = -kIdl$, where k is a constant depending only upon the wavelength and upon the nature of the absorbing medium. If I_o denotes the intensity of the incident light, there when $l = o$, $I_o = I$ = constant. Thus, the intensity of the light after it has passed through a solution of thickness l is:

$$I = I_o e^{-kl}. \qquad (12)$$

Taking into consideration the concentration c of the absorbing solution, the equation becomes:

$$I = I_o\, e^{-klc}. \qquad (13)$$

If the solution has another absorbing component its equation will be:

$$I_I = I_o\, e^{-k'l'c'}. \qquad (14)$$

Since the total transmission is the product of the separate transmissions, we have for the actual transmission of the solution:

$$I/I_{\ } = e^{-klc-k'l'c'},$$

$$\text{or } \ln (I/I_o) = -klc - k'l'c'. \qquad (16)$$

If the depth of the solution is a constant (20 mm. of solution was employed in all the methyl orange determinations) then the equation becomes:

$$\ln (I/I_o) = -Kc - K'c'. \qquad (17)$$

This equation, then, expresses the relation between the percentage transmission for a given depth of solution containing two components of absorption, where c and c' are the concentrations of these two components. K and K′ are constants depending upon the wavelength and upon the nature of the absorbers themselves.

Applying the equation to the case of methyl orange, let c represent the concentration of the quinoid salt and c' the concentration of the azo-base. If we represent by T the total concentration of methyl orange in solution then the relation between c and c' is such that:

$$c' = (T - 2c).^1 \qquad (18)$$

so that equation (17) becomes:

$$\ln (I/I_o) = -Kc - K'(T - 2c). \qquad (19)$$

In a pure aqueous solution of methyl orange c = o, and thus equation (17) reduces to:

$$\ln (I/I_o)' = -K'c' = -K'T. \qquad (20)$$

[1] A dibasic acid was used (sulphuric acid).

In a solution of methyl orange containing sufficient acid to suppress hydrolysis completely $c' = 0$, and thus equation (17) reduces to:

$$\ln (I/I_o)'' = -Kc = -K\,T/2. \qquad (21)$$

From equations (19), (20), and (21), K and K′ can be eliminated. Solving for c we obtain:

$$c = \frac{T[\ln (I/I_o) - \ln (I/I_o)']}{2[\ln (I/I_o)'' - \ln (I/I_o)']}. \qquad (22)$$

Where $(I/I_o)'$ is the percentage transmission of the pure methyl orange solution for some given wavelength, $(I/I_o)''$ the percentage transmission of the solution containing an excess of acid for the same wavelength, and (I/I_o) the percentage transmission, for the same wavelength, of the solution whose quinoid salt concentration c is to be determined. The amount of azo-base is then given at once by (18).

Returning now to the fundamental hydrolysis equation (6) derived on page 18:

$$\frac{\overset{+}{H} \times AzOH}{Q^+} = \frac{K_w}{K_i} = K_{(hydrolysis)}$$

$\overset{+}{Q}$ is equal to twice the quinoid salt concentration c; AzOH is given by c'; and $\overset{+}{H}$ is given by $2(T' - c)$, where T' represents the total quantity of acid added. The ionization of the salt in these extremely dilute solutions is assumed to be complete. The presence of the $NaSO_3$—group in the methyl orange molecule can have little effect upon the hydrogen ion concentration since benzene sulphonic acid itself is a strong acid, being dissociated to the extent of 90% at 25° for dilution $v = 32$[1].

In Table III are given the values of the hydrolysis product, (K_w/K_i), and also of the ionization constant K_i of methyl orange as a base; these values being calculated from equation (6) page 18. The concentration c of the quinoid salt was calculated from equation (22) page 22. The solutions investigated are those given on page 19, and the percentage transmissions for a depth equal to 20 mm. of the same solutions are given in Table II.

[1] Carnegie Monograph, Pub. No. 190, pg. 62.

The generally accepted value of the ion product for water is 1.2×10^{-14} at 25°. This work was carried out at an average temperature of 20°, and therefore it was necessary to know the ion product for water at 20°. This was found to be 0.81×10^{-14} at 20° by means of the well-known Van't Hoff formula:

$$\ln \frac{K_1}{K_2} = \frac{q\,(T_2 - T_1)}{R(T_2 \times T_1)} \qquad (23)$$

Where K_1 and K_2 are the constants for water at temperatures T_1 and T_2; R is the gas constant which equals 1.986 cal. per degree; and q is the heat of ionization of water or 13700 calories.

Table III

Solution.	λ = Å. U.	Azo-base $c' \times 10^4$.	Quinoid salt $c \times 10^5$.	$K_w/K_i \times 10^4$.	$K_i \times 10^{11}$.
II	5798	1.91	0.353	6.5	1.3
III	5748	1.84	0.716	6.1	1.3
	5797	1.80	0.897	4.4	1.8
	5847	1.82	0.813	5.1	1.6
IV	5748	1.75	1.16	5.2	1.6
	5797	1.69	1.46	3.7	2.2
	5847	1.74	1.23	4.8	1.7
V	5748	1.64	1.69	4.4	1.9
	5797	1.63	1.78	4.0	2.0
	5847	1.65	1.68	4.4	1.8
VI	5748	1.50	2.41	4.5	1.8
	5797	1.46	2.61	3.9	2.0
	5847	1.43	2.76	3.5	2.3
VII	5847	1.46	2.62	4.6	1.8
	5797	1.46	2.65	4.5	1.8
				Av., 4.5×10^{-4}	Av., 1.8×10^{-11}

The calculation of the hydrolysis and ionization constants from the percentage transmissions of the solutions is based on logarithmic functions. When the transmissions of the solutions are nearly complete, a variation in the percentage transmission of 1% can cause a variation of as much as 25% in the calculated constants[1]. The error involved in determining the transmissions of the solutions was about 1%.

The next determination was made on a much more dilute

1 Jour. Amer. Chem. Soc., 37, 795 (1915).

solution of methyl orange. The concentration of the mother solution of methyl orange was 1.9865×10^{-4} gram-molecules per liter; that of the mother solution of sulphuric acid 3.0885×10^{-4} gram-molecules per liter. The data for this determination follow:

Solutions

I 50 cc. methyl orange, diluted to 100 cc.
II 50 cc. methyl orange, 10 cc. sulfuric acid, diluted to 100 cc.
III 50 cc. methyl orange, 15 cc. sulfuric acid, diluted to 100 cc.
IV 50 cc. methyl orange, 20 cc. sulfuric acid, diluted to 100 cc.
V 50 cc. methyl orange, 1 cc. conc. sulfuric acid, diluted to 100 cc.
VI 50 cc. methyl orange, 0.5 cc. conc. sulfuric acid, diluted to 100 cc.
VII 50 cc. methyl orange, 0.2 cc. conc. sulfuric acid, diluted to 100 cc.
VIII 50 cc. methyl orange, 0.5 cc. conc. sulfuric acid, diluted to 100 cc.

The percentage transmissions for the above solutions are given in Table IV. Four determinations were made on the solution containing an excess of acid, in order to test whether the indicator was completely transformed into its red salt.

Table IV

	I/I_o for depth of solution = 20 mm.								Average
λ = Å. U.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	V, VI, VII and VIII.
5698	87.7	75.3	67.6	66.3	16.6	15.2	15.2	17.1	16.0
5723	88.9	80.7	74.2	72.3	20.1	20.1	20.2	---	20.1
5748	90.3	83.7	79.8	76.6	31.9	31.2	30.7	30.3	31.3
5773	91.6	---	81.7	81.3	38.8	39.0	39.5	41.1	39.9
5797	93.5	88.9	85.1	84.4	48.1	49.2	48.7	47.5	48.4
5823	94.5	91.3	87.0	86.2	55.3	53.8	55.0	56.4	55.1
5847	95.6	91.7	---	88.2	63.2	62.6	61.4	61.7	62.2

The constants calculated from the transmissions recorded in Table IV are given in Table V.

Table V

Solution.	λ = Å.U.	Azo-base $c' \times 10^5$.	Quinoid salt $c \times 10^6$.	$K_w/K_i \times 10^4$.	$K_i \times 10^{11}$.
IV------	5698	8.30	8.14	5.5	1.5
	5723	8.55	6.88	6.8	1.2
	5748	8.41	7.62	6.0	1.4
	5773	8.49	7.18	6.4	1.3
	5797	8.42	7.56	6.0	1.4
	5823	8.22	8.56	5.1	1.6
	5847	8.06	9.36	4.5	1.8
III------	5698	8.42	7.58	4.3	1.9
	5723	8.72	6.03	5.8	1.4
	5748	8.78	5.76	6.2	1.3
	5773	8.55	6.88	4.9	1.7
	5797	8.54	6.95	4.8	1.7
	5823	8.40	7.63	4.3	1.9
II------	5698	9.04	4.47	5.3	1.5
	5723	9.28	3.24	7.9	1.0
	5748	9.22	3.53	7.1	1.1
	5797	9.20	3.62	6.9	1.2
	5823	9.28	3.22	8.0	1.0
	5847	8.96	4.84	4.8	1.7
				Av., 5.8×10^{-4}	Av., 1.5×10^{-11}

The ionization constants recorded in Tables III and V by no means represent the limit of accuracy of the radiometric method. These measurements were made during the day when the building was in a continuous state of vibration, which seriously interfered with the accurate reading of the radiomicrometer deflections. The temperature which prevailed at the time these measurements were taken was somewhat higher than 20°. The constants were calculated for 20°; therefore the constants recorded in Tables III and V should be somewhat higher.

In order to determine the limit of accuracy of the radiometric method, a determination was made at night when the building was fairly free from vibrations. The temperature at the time of measurement was 20°. The concentration of the stock solution of methyl orange used was 3.054×10^{-4} gram-molecules per liter; that of the mother solution of sul-

phuric acid 3.089×10^{-4} gram-molecules per liter. The data for this determination follow:

Solutions

I 50 cc. methyl orange, diluted to 100 cc.
II 50 cc. methyl orange, 10 cc. sulfuric acid, diluted to 100 cc.
III 50 cc. methyl orange, 15 cc. sulfuric acid, diluted to 100 cc.
IV 50 cc. methyl orange, 20 cc. sulfuric acid, diluted to 100 cc.
V 50 cc. methyl orange, 25 cc. sulfuric acid, diluted to 100 cc.
VI 50 cc. methyl orange, 40 cc. sulfuric acid, diluted to 100 cc.
VII 50 cc. methyl orange, 0.7 cc. conc. sulfuric acid, diluted to 100 cc.
VIII 50 cc. methyl orange, 0.8 cc. conc. sulfuric acid, diluted to 100 cc.

Table VI

I/I_o for depth of solution = 20 mm. Temperature = 20°.

λ = Å. U.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	Average VII and VIII
5723	88.2	71.8	63.7	58.0	51.6	---	11.8	11.6	11.7
5748	90.0	77.6	68.6	64.0	59.8	---	17.1	17.6	17.4
5773	91.6	---	75.2	71.0	67.4	---	24.8	24.9	24.9
5797	93.4	---	78.7	76.2	72.6	63.8	32.5	33.2	32.4
5848	95.4	89.6	86.6	84.5	---	75.2	49.0	49.8	49.4
5898	97.2	---	91.4	89.8	88.7	---	63.5	63.5	63.5

The constants calculated from Table VI are recorded in Table VII.

Table VII

Solution	λ = Å. U.	Azo-base $c' \times 10^4$.	Quinoid salt $c \times 10^5$.	$K_w/K_i \times 10^4$.	$K_i \times 10^{11}$.
VI	5797	0.975	2.76	3.4	2.4
	5848	0.975	2.76	3.4	2.4
V	5723	1.193	1.67	4.3	1.9
	5748	1.147	1.99	3.5	2.3
	5773	1.167	1.80	3.8	2.1
	5797	1.203	1.62	4.5	1.8
	5898	1.197	1.65	4.4	1.8
IV	5723	1.211	1.58	3.5	2.3
	5748	1.211	1.58	3.5	2.3
	5773	1.227	1.50	3.8	2.1
	5798	1.235	1.46	4.0	2.0
	5848	1.315	1.36	4.7	1.8
	5898	1.245	1.42	4.2	1.9
III	5723	1.281	1.23	3.5	2.3
	5748	1.277	1.25	3.5	2.3
	5773	1.295	1.16	3.9	2.1
	5798	1.269	1.24	3.5	2.3
	5848	1.309	1.09	4.3	1.9
	5898	1.301	1.13	4.0	2.0
II	5723	1.372	0.773	4.1	2.0
	5748	1.390	0.687	4.9	1.7
	5848	1.383	0.718	4.6	1.8
				Av., 4.0×10^{-4}	Av., 2.1×10^{-11}

The determination of the percentage transmissions from which the constants recorded in Table VII are calculated was made under the most favorable conditions. The average constant 2.1×10^{-11}, therefore, more likely represents the true constant of the indicator.

Phenolphthalein

Regarding phenolphthalein as a monobasic acid, the dynamic condition of equilibrium may be represented[1]:

$$\frac{\bar{Q} \times \overset{+}{H}}{LH} = K_i, \qquad (24)$$

where $\bar{Q}$ is the concentration of the colored quinoid ions, and LH is the concentration of the colorless lactoid molecules. Dividing this by the ion product for water:

$$\frac{LH \times \bar{O}H}{Q^+} = \frac{K_w}{K_i}. \qquad (25)$$

The application of the method developed for methyl orange is much simpler since colored solutions of phenolphthalein contain one component of absorption only. The pure water solution of phenolphthalein is perfectly transparent. A large excess of alkali converts the colorless lactoid molecules completely into the colored quinoid salt. If we represent by c the concentration of the quinoid salt in solution, then the percentage transmission of the solution will be given by:

$$\ln (I/I_o) = -Kc \qquad (26)$$

Let the total concentration of indicator in solution be T. In solutions containing a large excess of alkali, the indicator will exist entirely as the colored quinoid salt when $T = c$. The transmission of such a solution will be given by:

$$\ln (I/I_o)' = -KT \qquad (27)$$

Eliminating K from (26) and (27) and solving for c, we have:

$$c = \frac{T \times \ln (I/I_o)}{\ln (I/I_o)'} \qquad (28)$$

1 See page 18.

Where (I/I_o) is the percentage transmission, for some given wavelength of light of the solution under investigation, $(I/I_o)'$ is the percentage transmission of the solution containing a large excess of alkali for the same wavelength of light. The concentration of the colorless lactoid molecules is given at once by $(T - c)$. The hydroxyl ion concentration was varied by the addition of ammonium hydroxide and ammonium chloride. The OH ion concentration was determined in the following manner:

$$\frac{\overset{+}{NH_4} \times \overset{-}{OH}}{(NH_4OH + NH_3)} = K_b. \qquad (29)$$

If we represent by S the concentration of the ammonium chloride, and by B the total concentration of ammonia in solution, then since NH_4^+ ions are furnished almost entirely by the ammonium chloride, and since the ammonium hydroxide is practically undissociated especially in the presence of a common ion:

$$\overset{-}{OH} = \frac{K_b \times B}{S}. \qquad (30)$$

The constant K_b for ammonia is given[1] as 18×10^{-6} at 25°. Since the work on phenolphthalein was done at 20°, K_b was reduced to 20° by means of equation (23). The value obtained was $K_b = 17.4 \times 10^{-6}$, q being taken as 1400 calories.

Preparation of Solutions: A pure sample of phenolphthalein was recrystallized from absolute methyl alcohol. A weighed amount of this purified product (about 1 gram) was dissolved in 50 cc. of absolute ethyl alcohol. A small volume of this solution (about 1 cc.) was then diluted to 2000 cc. with conductivity water. These small volumes were measured by means of accurately calibrated pipettes of very small bore. The solution of ammonium hydroxide employed was distilled from barium hydroxide in order to eliminate carbon dioxide. All solutions were prepared with conductivity water, and especial care was taken to protect these solutions from the carbon dioxide of the air.

[1] Carnegie Institution of Washington, Pub. No. 63., 298.

Since the presence of an excess of alkali causes a rather rapid fading in the color of the phenolphthalein solutions[1], the percentage transmissions of such solutions had to be taken immediately after the solutions were prepared. It was found that these solutions could be prepared and the percentage transmissions taken for five wavelengths of light within eight minutes. In this short interval of time the fading is only very slight[2].

Results with Phenolphthalein

The six solutions recorded below were prepared from the following mother solutions. The concentration of the phenolphthalein was 6.697×10^{-5} gram molecules per liter; the ammonium hydroxide was 0.1448 normal, and the ammonium chloride solution 0.1 normal:

Solutions

I 75 cc. phenolphthalein, diluted to 100 cc.
II 75 cc. phenolphthalein, 2 cc. NH_4OH, 1 cc. NH_4Cl, diluted to 100 cc.
III 75 cc. phenolphthalein, 2 cc. NH_4OH, 2 cc. NH_4Cl, diluted to 100 cc.
IV 75 cc. phenolphthalein, 2 cc. NH_4OH, 5 cc. NH_4Cl, diluted to 100 cc.
V 75 cc. phenolphthalein, 2 cc. NH_4OH, 10 cc. NH_4Cl, diluted to 100 cc.
VI 75 cc. phenolphthalein, 1 cc. *N*NaOH, diluted to 100 cc.

The percentage transmissions for a depth equal to 20 mm. of each of these solutions are recorded in Table VIII. The hydroxyl ion concentrations, the concentrations of the colored quinoid salt and of the colorless lactoid form, and the hydrolysis and ionization constants of the indicator calculated from Table VIII are recorded in Table IX.

Table VIII

I/I_o for depth of solution = 20 mm. Temperature = 20°.

λ = Å. U.	I.	II.	III.	IV.	V.	VI.
5773	100.0	30.8	46.3	70.7	---	10.1
5798	100.0	37.8	53.4	76.3	86.7	14.3
5823	100.0	45.3	58.9	78.5	89.3	20.2
5848	100.0	51.7	66.2	83.0	91.3	27.4
5948	100.0	---	83.7	---	---	57.7

[1] McCoy: Amer. Chem. Jour., 31, 516 (1904).
[2] See also Jour. Amer. Chem. Soc., 37, 800 (1915), for a fuller discussion.

Table IX

Solutions.	λ = Å. U.	Lactoid form $c \times 10^5$.	Quinoid salt $c \times 10^5$.	$OH \times 10^5$.	$K_w/K_i \times 10^5$.	$K_i \times 10^{10}$.	Average $K_i \times 10^{10}$.
II----	5773	2.44	2.58	5.039	4.77	1.70	---
	5798	2.51	2.51	5.039	5.05	1.60	1.63
	5823	2.54	2.48	5.039	5.17	1.57	---
	5848	2.46	2.56	5.039	4.85	1.67	---
III----	5773	3.33	1.69	2.519	4.96	1.64	---
	5798	3.40	1.62	2.519	5.27	1.54	---
	5823	2.35	1.67	2.519	5.06	1.60	1.56
	5848	3.42	1.60	2.519	5.38	1.51	---
	5948	3.40	1.62	2.519	5.28	1.53	---
IV----	5773	4.26	0.757	1.007	5.68	1.43	---
	5798	4.32	0.696	1.007	6.27	1.20	1.38
	5823	4.26	0.761	1.007	5.63	1.44	---
	5848	4.30	0.720	1.007	6.02	1.35	---
V----	5798	4.65	0.369	0.503	6.37	1.27	---
	5823	4.67	0.356	0.503	6.63	1.22	1.23
	5848	4.67	0.352	0.503	6.68	1.21	---

For the next determination, the results of which are recorded in Tables X and XI, the concentration of the mother solution of phenolphthalein was 4.603×10^{-5} gram-molecules per liter. The concentrations of the mother solutions of ammonia and ammonium chloride were the same as for the previous determination.

Solutions

I 75 cc. phenolphthalein, 1 cc. NH_4OH, 0.5 cc. NH_4Cl, diluted to 100 cc.
II 75 cc. phenolphthalein, 1 cc. NH_4OH, 1 cc. NH_4Cl, diluted to 100 cc.
III 75 cc. phenolphthalein, 1 cc. NH_4OH, 2 cc. NH_4Cl, diluted to 100 cc.
IV 75 cc. phenolphthalein, 1 cc. NH_4OH, 2.5 cc. NH_4Cl, diluted to 100 cc.
V 75 cc. phenolphthalein, 0.8 cc. *N*NaOH, diluted to 100 cc.

Table X

I/I_o for depth of solution = 20 mm. Temperature 20°.

λ = Å. U.	I.	II.	III.	IV.	V.
5773	48.2	62.2	73.0	81.3	15.7
5798	54.2	66.3	78.7	83.0	22.7
5823	59.6	70.7	83.9	86.0	30.5
5848	66.4	74.6	85.1	89.0	37.9
5948	84.8	87.7	---	94.8	62.2

Table XI

Solution.	λ = Å. U.	Lactoid form $c \times 10^5$.	Quinoid salt $c \times 10^5$.	OH $\times 10^5$.	$K_w/K_i \times 10^5$.	$K_i \times 10^{10}$.	Average $K_i \times 10^{10}$.
I----	5773	2.09	1.36	5.039	7.79	1.04	---
	5798	2.03	1.42	5.039	7.24	1.12	1.14
	5823	1.95	1.50	5.039	6.56	1.23	---
	5848	1.99	1.46	5.039	6.92	1.17	---
II----	5773	2.56	0.884	2.519	7.31	1.11	---
	5798	2.49	0.953	2.519	6.61	1.23	---
	5823	2.44	1.006	2.519	6.13	1.32	1.25
	5848	2.41	1.040	2.519	5.83	1.39	---
	5948	2.49	0.951	2.519	6.61	1.23	---
III----	5773	2.86	0.587	1.259	6.15	1.32	---
	5798	2.89	0.557	1.259	6.53	1.24	1.21
	5823	2.94	0.508	1.259	7.96	1.02	---
	5848	2.87	0.573	1.259	6.37	1.27	---
IV----	5773	3.05	0.386	1.007	8.03	1.01	---
	5798	3.01	0.433	1.007	7.01	1.15	---
	5823	3.01	0.436	1.007	7.01	1.15	1.06
	5848	3.03	0.413	1.007	7.42	1.09	---
	5948	3.06	0.385	1.007	8.04	1.01	---

The concentrations of the mother solutions used in the preparation of the solutions for the following determination, were the same as those used for the first determination. The results are recorded in Tables XII and XIII.

Solutions

I 75 cc. phenolphthalein, 0.5 cc. NH_4OH, 0.5 cc. NH_4Cl, diluted to 100 cc.
II 75 cc. phenolphthalein, 0.5 cc. NH_4OH, 1 cc. NH_4Cl, diluted to 100 cc.
III 75 cc. phenolphthalein, 0.5 cc. NH_4OH, 2 cc. NH_4Cl, diluted to 100 cc.
IV 75 cc. phenolphthalein, 0.8 cc. *N*NaOH, diluted to 100 cc.

Table XII

I/I_o for depth of solution = 20 mm. Temperature = 20°.

λ = Å. U.	I.	II.	III.	IV.
5773	63.2	76.2	87.3	9.9
5798	65.8	80.3	89.2	14.7
5823	72.0	82.8	91.5	20.4
5848	74.3	---	---	27.4
5948	88.8	93.3	---	57.6

Table XIII

Solution.	λ = Å. U.	Lactoid form $c \times 10^5$.	Quinoid salt $c \times 10^5$.	$OH \times 10^5$.	$K_w/Ki \times 10^5$.	$K_i \times 10^{10}$	Average $K_i \times 10^{10}$.
I----	5773	4.026	0.99	2.519	10.16	0.80	---
	5798	3.935	1.09	2.519	9.07	0.99	---
	5823	3.985	1.04	2.519	9.65	0.83	0.89
	5848	3.875	1.15	2.519	8.47	0.97	---
	5948	3.955	1.07	2.519	9.28	0.87	---
II----	5773	4.43	0.59	1.26	9.46	0.86	---
	5798	4.45	0.57	1.26	9.77	0.83	0.87
	5823	4.42	0.60	1.26	9.24	0.88	---
	5948	4.39	0.62	1.26	8.82	0.92	---
III----	5773	4.73	0.30	0.63	10.07	0.81	---
	5798	4.73	0.30	0.63	10.00	0.81	0.79
	5823	4.74	0.28	0.63	10.65	0.75	---

A consideration of the separate tables will show that the constant K_i decreases with decreasing hydroxyl ion concentrations. This is in accord with the results of previous investigators. Wegscheider[1] concludes that this variation may be accounted for by regarding phenolphthalein as a diabasic acid, and in fact the salts $C_{20}H_{12}O_4Na_2$ and $C_{20}H_{12}O_4K_2$ have actually been prepared. Rosenstein[2] confirms this conclusion, and furthermore shows that it is only when the second hydrogen of the indicator acid is replaced by the base that the colored form is produced in appreciable quantity. The assumption, then, that phenolphthalein acts as a monobasic acid does not hold.

Considerable variation will also be observed when the values of the constants given by each of the three tables are compared. The average value for K_i given by Table IX is 1.45×10^{-10}; the average for Table XI is 1.16×10^{-10}, and for Table XIII, 0.85×10^{-10}. That the concentration of the indicator is not a factor in this variation of the constants may be shown by the following. Considering again equation 25:

$$\frac{LH \times \overline{OH}}{Q^+} = \frac{K_w}{K_i}$$

[1] Loc. cit.
[2] Loc. cit.

(Q^+) and (LH) are given by equation 28:

$$\frac{\ln (I/I_o) \times T}{\ln (I/I_o)'} = Q.$$

$$\text{and } LH = (T - \overset{+}{Q}) = T - \frac{\ln (I/I_o) \times T}{\ln (I/I_o)'}.$$

Substituting these values in the hydrolysis equation, and eliminating T, which is the total concentration of the indicator in solution:

$$\frac{OH[\ln (I/I_o)' - \ln (I/I_o)]}{\ln (I/I_o)} = \frac{K_w}{K_i}.$$

The calculation of the ionization constant is independent, then, of the concentration of the indicator employed. The variation in the average constants given by Tables IX, XI and XIII must therefore be due to other causes. This variation is beyond a doubt due to the effect of the neutral salt present in solution. Rosenstein[1] has made a very careful study of the effect of neutral salt upon the fraction of the indicator transformed, and, correspondingly, upon its ionization constant. He found that the value of the constant is doubled by increasing the neutral salt concentration from 0.03 to 0.40 normal. Results of the same character are shown by a comparison of the various tables. When the ratio of ammonium hydroxide to ammonium chloride remains the same, *i. e.*, when the hydroxyl ion concentration remains the same, the constants are larger the greater the amount of ammonium chloride present. Thus, when the ratio of ammonium hydroxide to ammonium chloride is 1 to 1, solution 3, Table IX, which is 2×10^{-5} *N.* with respect to ammonium chloride, gives a constant 1.56×10^{-10}; solution 2, Table XI, which is 1×10^{-5} *N.* with respect to ammonium chloride, gives a constant 1.25×10^{-10}. The effect, then, of increasing concentrations of neutral salts is to increase the experimentally determined ionization constant.

[1] Loc. cit.

Summary

A very satisfactory system of apparatus was constructed by means of which it was possible to quickly and accurately measure the percentage transmission for any given depth of solution for wavelengths of light from $\lambda = 0.4\ \mu$ to $\lambda = 1.2\ \mu$.

A new method was developed for determining the ionization constants of indicators. This method serves as well for a two-colored as for a one-colored indicator.

The ionization constant for methyl orange considered as a base was found to be 2.1×10^{-11}.

The method was applied to phenolphthalein on the assumption that the indicator acts as a monobasic acid. It was found that the ionization constant decreases with decreasing hydroxyl ion concentrations. The assumption, then, that phenolphthalein acts as a monobasic acid is untenable.

As has been previously shown by Rosenstein, neutral salts have great effect upon the experimentally determined ionization constants. The constants increase with increasing concentrations of neutral salt.

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BIOGRAPHY

THE author of this dissertation was born in Baltimore, Maryland, September 25, 1891. After graduating from the High School of Baltimore City in June, 1908, he entered the Johns Hopkins University in the Fall of the same year. In June, 1912, he received the degree of Bachelor of Arts from the Johns Hopkins University. The following Autumn he entered the Department of Chemistry in this University, taking Physical Chemistry and Applied Electricity as his subordinate subjects. During the first two years of his graduate study he was appointed laboratory assistant to Dr. Lovelace. For the year 1914-1915 he was appointed Fellow in Chemistry.

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